

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 841 676 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
05.03.2003 Bulletin 2003/10

(51) Int Cl.7: **H01J 1/142**

(21) Application number: **97119574.8**

(22) Date of filing: **08.11.1997**

(54) Cathode for electron tube and method for manufacturing the same

Kathode für eine Elektronenröhre und Herstellungsverfahren

Cathode pour un tube à électrons et procédé de fabrication

(84) Designated Contracting States:
DE FR GB IT NL SE

(30) Priority: **12.11.1996 JP 30002496**
12.11.1996 JP 30002596

(43) Date of publication of application:
13.05.1998 Bulletin 1998/20

(73) Proprietor: **MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD.**
Kadoma-shi, Osaka (JP)

(72) Inventors:

- **Hayashida, Yoshiaki**
Takaishi-shi, Osaka 592 (JP)
- **Ozawa, Tetsuro**
Takatsuki-shi, Osaka 569 (JP)
- **Sakurai, Hiroshi**
Takatsuki-shi, Osaka 569 (JP)
- **Kawasaki, Masaki**
Toyonaka-shi, Osaka 560 (JP)

(74) Representative:
Schwarzensteiner, Marie-Luise, Dr. et al
Grape & Schwarzensteiner
Patentanwälte
Sebastiansplatz 7
80331 München (DE)

(56) References cited:
EP-A- 0 330 355 **EP-A- 0 373 701**
GB-A- 663 981 **GB-A- 700 313**

- **PATENT ABSTRACTS OF JAPAN** vol. 014, no. 120 (E-0899), 6 March 1990 & JP 01 315926 A (MITSUBISHI ELECTRIC CORP), 20 December 1989,
- **PATENT ABSTRACTS OF JAPAN** vol. 013, no. 074 (E-717), 20 February 1989 & JP 63 257153 A (MITSUBISHI ELECTRIC CORP), 25 October 1988,

EP 0 841 676 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

[0001] The present invention relates to a cathode for electron tubes such as cathode-ray tubes (CRT) used for television or information displays.

[0002] As shown in FIG. 14, a conventional cathode for an electron tube includes a heater coil 101, a cylindrical sleeve 102 with the built-in heater coil 101, a metal substrate 103, containing nickel as a main component and a trace of reducing elements such as magnesium, at one opening of the sleeve 102, and an emissive material layer 104 adhered onto the substrate 103. For the emissive material layer 104, a material that includes as a main component an alkaline earth metal oxide containing barium is used as an oxide cathode. A phenomenon is found that the emission current of such a cathode gradually decreases after long operation of several thousand hours due to the deterioration of emissive materials.

[0003] Therefore, a proposal has been tested to improve the life of a cathode by adding from 0.3 wt. % to 15 wt. % of rare earth metals such as scandium oxide and yttrium oxide to an emissive material layer (Japanese Laid-open Patent Publication No. 62-22347).

[0004] Another proposal also has been tested whereby zirconium oxide or hafnium oxide is added to an emissive material layer at from 0.1 wt. % to 10 wt. % so as to extend the life of a cathode (Japanese Laid-open Patent Publication No. 2-195628).

[0005] Due to the recent increase in current density accompanied by the improvement of CRT display properties, there is a problem in that more and more load is added to a cathode, shortening the life of the cathode. Thus, a cathode has been demanded that has a longer life than conventional cathodes.

[0006] It is, therefore, an object of the present invention to provide a long-life cathode - particularly, a cathode for an electron tube that has little decrease in emission current after long operation and has a sufficient life even if the current density is further increased in a CRT, and to provide a long-life and economical cathode for an electron tube.

[0007] The present invention provides a cathode according to claim 1 for an electron tube in which an emissive material, having particles that include the oxide of an alkaline earth metal as a main component and at least one element selected from the group consisting of titanium, zirconium and hafnium, is adhered onto a metal substrate including nickel as a main component.

[0008] The present invention also provides a cathode according to claim 6 for an electron tube in which an emissive material, having particles that include the oxide of an alkaline earth metal as a main component and at least one element selected from the group consisting of vanadium, niobium and tantalum, is adhered onto a metal substrate including nickel as a main component.

[0009] In the present invention, a long-life cathode for an electron tube is provided. Particularly, by adding,

along with the oxide of an alkaline earth metal, at least one element selected from the group consisting of titanium, zirconium and hafnium to the emissive material of a cathode, the properties of the emissive material improve, especially in reducing the deterioration of the emission current under high current density. Also, an economical and long-life cathode with long emission current stability is provided by adding, along with the oxide of an alkaline earth metal, at least one element selected from the group consisting of vanadium, niobium and tantalum to the emissive material of the cathode.

[0010] The present invention provides a method for manufacturing a cathode for an electron tube according to claim 12, including the step of thermally decomposing

carbonate containing at least one element selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium and tantalum and an alkaline earth metal so as to adhere an emissive material, containing the oxide of the alkaline earth metal as a main component

and the above-noted element, onto a metal substrate including nickel as a main component. In this method, the element such as titanium is evenly provided in each particle of the alkaline earth metal oxide, so that a cathode with even emissive properties and stability is provided.

[0011] A first cathode of the present invention has an emissive material, comprising particles containing the oxide of an alkaline earth metal as a main component and at least one element selected from the group consisting of titanium, zirconium and hafnium, adhered onto a metal substrate including nickel as a main component.

[0012] It is preferable in the first cathode that the total content of at least one element selected from the group consisting of titanium, zirconium and hafnium is from 0.001 wt. % to 1 wt. %, or more preferably from 0.001 wt. % to 0.1 wt. %, relative to the total weight of the emissive material. Therefore, the emissive properties of the cathode improve. The cathode can be used under high current density.

[0013] It is also preferable in the first cathode that the emissive material further comprising particles of an alkaline earth metal oxide. Thus, as described above, the cathode has improved emissive properties, and can be used under high current density. More specifically, it is

preferable that the emissive material comprising the mixture of the particles containing the oxide of an alkaline earth metal as a main component and at least one element selected from the group consisting of titanium, zirconium and hafnium and the particles of an alkaline earth metal oxide. In this case, it is preferable that the particles containing the oxide of an alkaline earth metal as a main component and at least one element selected from the group consisting of titanium, zirconium and hafnium are included at 20 wt. % to 80 wt. % relative to the total weight of the emissive material. As a result, the emissive properties of the cathode further improve.

[0014] A second cathode of the present invention has an emissive material comprising particles, containing

the oxide of an alkaline earth metal as a main component and at least one element selected from the group consisting of vanadium, niobium and tantalum, adhered onto a metal substrate including nickel as a main component.

[0015] It is preferable in the second cathode that the content of the above-mentioned element is from 0.001 wt. % to 5 wt. % relative to the total weight of the emissive material when the element is included as a metal. Thus, the emission current is stabilized for a long period, and the life of the cathode increases.

[0016] It is also preferable in the second cathode that the content of the element is from 0.002 wt. % to 6 wt. % relative to the total weight of the emissive material when the element is included as an oxide. Therefore, as mentioned above, the emission current would be stabilized for a long period, and an economical and long-life cathode is provided. In this case, it is further preferable that the oxide is in the form of particles having an average particle diameter of 10 μm or less, so that the emission current further stabilizes for a long period.

[0017] The method of the present invention includes the step of thermally decomposing carbonate, containing at least one element selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium and tantalum and an alkaline earth metal, so as to adhere the particles of an emissive material, containing the oxide of the alkaline earth metal as a main component and the element mentioned above, onto a metal substrate including nickel as a main component. In this method, the element such as titanium is evenly provided in each particle of the alkaline earth metal oxide, so that a cathode with even emissive properties and stability is provided.

[0018] It is preferable in the method that the method further includes the step of coprecipitating, from a solution including the nitrate of at least one element selected from the group consisting of titanium and zirconium and the nitrate of an alkaline earth metal, the above-mentioned element and alkaline earth metal as carbonate. By this method, the residual impurities in the emissive material are significantly reduced, so that a decrease in emissive properties from impurities would be prevented.

[0019] In this case, it is further preferable that the above-mentioned element and alkaline earth metal are coprecipitated as carbonate by mixing the solution containing the nitrate mentioned above with a solution including a carbonate ion (more preferably, a solution containing at least one salt selected from the group consisting of the carbonate of an alkaline metal, the hydrogen-carbonate of an alkaline metal, ammonium carbonate and ammonium hydrogencarbonate).

[0020] In the accompanying drawings:

FIG. 1 is a cross-sectional view showing an embodiment of a schematic structure of a cathode of the present invention;

FIG. 2 is a cross-sectional view showing another

embodiment of a schematic structure of a cathode of the present invention;

FIG. 3 is a cross-sectional view showing another embodiment of a schematic structure of an improved cathode which is not claimed;

FIG. 4 is a graph showing the change in emission current with time in an embodiment of a cathode of the present invention;

FIG. 5 is a graph showing the relationship between the content of zirconium and the change in emission current in an embodiment of a cathode of the present invention;

FIG. 6 is a graph showing the change in emission current with time in an embodiment of a cathode of the present invention;

FIG. 7 is a graph showing the change in emission current with time in an embodiment of a cathode of the present invention;

FIG. 8 is a graph showing the relationship between the content of vanadium or vanadium oxide and the change in emission current in an embodiment of a cathode of the present invention;

FIG. 9 is a graph showing the change in cut-off voltage with time in an embodiment of a cathode of the present invention;

FIG. 10 is a graph showing the change in emission current with time in an embodiment of a cathode of the present invention;

FIG. 11 is a graph showing the relationship between the particle diameters of tantalum oxide and the change in emission current in an embodiment of a cathode of the present invention;

FIG. 12 is a graph showing the change in emission current with time in an embodiment of a cathode of the present invention;

FIG. 13 is a graph showing the change in emission current with time in an embodiment of a cathode of the present invention; and

FIG. 14 is a cross-sectional view showing an embodiment of a schematic structure of a conventional cathode.

[0021] The preferred embodiments of the present invention are now explained using the figures.

[0022] FIG. 1 shows a schematic structure of one embodiment of a cathode of the present invention. The cathode includes a heater coil 1, a cylindrical sleeve 2 with the built-in heater coil 1, a metal substrate 3 that contains nickel as a main component and a trace of reducing elements such as magnesium positioned at one opening of the sleeve 2, and an emissive material layer, comprising particles 5 containing barium and an alkaline earth metal oxide as a main component, adhered onto the substrate 3. Each particle includes at least one element selected from the group consisting of titanium, zirconium and hafnium.

[0023] FIG. 2 shows a schematic structure of another embodiment of a cathode of the present invention. In

this case, an emissive material layer comprises particles 5, containing an alkaline earth metal oxide as a main component and titanium and the like, and particles 6 of alkaline earth metal oxides.

[0024] Therefore, the emissive material layers shown in FIG. 1 and FIG. 2 that are adhered onto a substrate as the particles 5 and 6 are different from the conventional emissive material layer 4 shown in FIG. 14.

[0025] FIG. 3 shows a schematic structure of another embodiment of an improved cathode. As in FIG. 1, the cathode shown in FIG. 3 includes a heater coil 1, a cylindrical sleeve 2 with the built-in heater coil 1, a metal substrate 3 that contains nickel as a main component and a trace of reducing elements such as magnesium positioned at one opening of the sleeve 2, and an emissive material layer including an alkaline earth metal oxide 7 containing barium and at least one metal selected from the group consisting of vanadium, niobium and tantalum (or an oxide thereof) 8, adhered onto the substrate 3.

[0026] The present invention is explained in further detail by referring to the following examples, which are not intended to limit this invention.

Example 1

[0027] Zirconium nitrate was dissolved in a solution of alkaline earth metal nitrate, including barium nitrate and strontium nitrate, so as to have a content of zirconium atoms of 0.02 mole % (mole ratio relative to the entire amount of alkaline earth metal), thus preparing a mixed solution. A solution of sodium carbonate was added to this mixed solution, thereby preparing ternary (barium/strontium/zirconium) coprecipitated carbonate particles in which each particle includes zirconium atoms at an average of 0.02 mole %. Instead of zirconium nitrate, zirconium (IV) dinitrate oxide may be used. Similarly, the carbonate or the hydrogencarbonate of an alkaline metal, ammonium carbonate, or ammonium hydrogencarbonate may be used instead of sodium carbonate.

[0028] The ternary coprecipitated carbonate particles were adhered onto a cathode substrate in a thickness of about 50 μm , and were thermally decomposed in a vacuum at 930°C. As a result, a cathode having the same structure as in FIG. 1 was provided that had an emissive material layer including ternary (barium/strontium/zirconium) oxide particles (with 0.015 wt. % average content of zirconium).

[0029] In the above-mentioned method for manufacturing the cathode, titanium nitrate or hafnium chloride was used instead of zirconium nitrate so as to provide a cathode having the same structure as in FIG. 1 and having an emissive material layer including barium/strontium/titanium or barium/strontium/hafnium oxide particles with 0.015 wt. % average content of titanium atoms or hafnium atoms.

[0030] The cathode prepared as described above was used in a CRT for displays, and an accelerated life

test was carried out for 2,000 hours while the current density of the CRT was set at 2.0A/cm² at the beginning of the operation.

[0031] FIG. 4 shows the change in emission current with time in the accelerated life test. Line A in the figure shows the result in the case of the cathode having an emissive material layer including barium/strontium/titanium coprecipitated oxide particles; line B indicates the result in the case of the cathode having an emissive material layer including barium/strontium/zirconium coprecipitated oxide particles; line C shows the result in the case of the cathode having an emissive material layer including barium/strontium/hafnium coprecipitated oxide particles; and line (a) indicates the result in the case of a conventional cathode having an emissive material layer containing the particles of an alkaline earth metal oxide.

[0032] As clearly shown in FIG. 4, the decrease in emission current of the cathode by the accelerated life test is smaller than that of the conventional cathode when titanium, zirconium or hafnium is included in each particle of the alkaline earth metal oxide, thus improving the life of the cathode. Particularly, when the particles of an alkaline earth metal oxide in which titanium or zirconium is coprecipitated are used for an emissive material layer, the decrease in emission current would be reduced significantly. This is because nitrate is used as a material in preparing carbonate particles, so that much less residual impurities are found in the emissive material layer than in the case of using the chlorides as a starting material. (The impurities are chlorine when using chloride as a starting material.)

[0033] Also, conventional cathodes require several minutes to stabilize the emission current after electric discharge begins. During this period, a phenomenon (called emission slump) of gradually decreasing emission current is found. The emission slump of the cathode prepared by coprecipitating zirconium or hafnium is about half as much as that of conventional cathodes, thus providing a highly stable electron emission. Therefore, in order to improve the life of a cathode and also reduce the emission slump, it is preferable that zirconium is coprecipitated in preparing carbonate particles.

[0034] As shown in FIG. 5, the effect of increasing the life of a cathode is found when the content of titanium, zirconium or hafnium is from 0.001 wt. % to 1 wt. %, more preferably from 0.001 wt. % to 0.1 wt. %, relative to the total weight of the emissive material layer.

[0035] Although binary (barium/strontium) alkaline earth metals were used for oxide particles in this example, the same effects were also found in using ternary (barium/strontium/calcium) alkaline earth metals. This is also true in the following examples.

Example 2

[0036] Zirconium nitrate was dissolved in a solution of alkaline earth metal nitrate, including barium nitrate and

strontium nitrate, at 0.04 mole % relative to the entire alkaline earth metal (at 0.03 wt. % relative to the particles of the alkaline earth metal oxide), thus preparing a mixed solution. A solution of sodium carbonate was added to this mixed solution, thereby precipitating ternary (barium/strontium/zirconium) carbonate particles in which zirconium atoms are contained at an average of 0.04 mole %. On the other hand, a solution of sodium carbonate was added to a mixed solution of barium nitrate and strontium nitrate for precipitation, thus providing particles of binary (barium/strontium) carbonate.

[0037] The ternary carbonate particles and the binary carbonate particles were mixed at a 1:1 weight ratio so as to prepare a mixed material of carbonate particles containing zirconium and carbonate particles containing no zirconium. The mixed material was adhered onto a cathode substrate in a thickness of about 50 μm , and was thermally decomposed in a vacuum at 930°C. Thus, a cathode was provided that had an emissive material layer including the mixed material of ternary (barium/strontium/zirconium) oxide particles 5 and binary (barium/strontium) oxide particles 6 as shown in FIG. 2.

[0038] The cathode prepared as described above was used in a CRT for displays, and an accelerated life test was carried out for 2,000 hours while the current density of the CRT was set at 2.0A/cm² at the beginning of the operation.

[0039] FIG. 6 shows the change in emission current with time in the accelerated life test. In the figure, line D shows the result in the case of the cathode that has an emissive material layer including the mixed material of the ternary (barium/strontium/zirconium) oxide particles and the binary (barium/strontium) oxide particles; and line (b) shows the result in the case of the cathode that has an emissive material layer including only the mixed material of the ternary (barium/strontium/zirconium) oxide particles. As clearly shown in FIG. 6, the decrease in emission current of the cathode by the accelerated life test is reduced when an emissive material layer includes the mixed material of the oxide particles containing zirconium and those containing no zirconium, thus increasing the life of the tube. The same results were also obtained when titanium or hafnium was used instead of zirconium.

[0040] The effect of improving the life of a cathode was found when the particles of the alkaline earth metal oxide containing titanium, zirconium or hafnium were contained at 20 wt. % to 80 wt. % relative to the total weight of an emissive material layer.

Example 3 (not forming part of the present invention)

[0041] To binary carbonate containing barium and strontium at a 1:1 mole ratio, 0.8 wt. % (relative to the binary carbonate) of vanadium (1.1 wt. % relative to an emissive material layer) or 1.0 wt. % (relative to the binary carbonate) of vanadium oxide (1.3 wt. % relative to the emissive material layer) was added, thus prepar-

ing a mixed material of barium/strontium carbonate and vanadium or vanadium oxide. The mixed material was adhered onto a cathode substrate in a thickness of about 50 μm , and was thermally decomposed in a vacuum at 930°C. Thus, a cathode having the same structure as in FIG. 3 was provided that had an emissive material layer containing barium/strontium oxide and vanadium or vanadium oxide

[0042] The cathode prepared as described above was used in a CRT for displays, and an accelerated life test was carried out for 2,000 hours while the current density of the CRT was set at 2.0A/cm² at the beginning of the operation.

[0043] FIG. 7 shows the change in emission current with time in the accelerated life test. In the figure, line E shows the result in the case of the cathode in which vanadium was added to the emissive material layer; line F indicates the result in the case of the cathode in which vanadium oxide was added to the emissive material layer; and line (a) shows the result in the case of a conventional cathode in which an emissive material layer is made only of an alkaline earth metal oxide. Compared with the conventional cathode, the deterioration of emission current of the cathode by the accelerated life test is significantly reduced as clearly shown in FIG. 7 when vanadium or vanadium oxide is added to the emissive material layer, thereby increasing the life of the tube. Especially with the use of vanadium oxide, the effects are significant, with little decrease in emission current.

[0044] Also, vanadium and vanadium oxide can be obtained easily in the industry, and are economical. Thus, by adding vanadium or vanadium oxide to an emissive material layer, an economical and long-life cathode is provided.

[0045] As shown in FIG. 8, the effects of reducing the deterioration of emission current were obtained effectively when the contents of vanadium and vanadium oxide were 0.001 wt. % to 5 wt. % and 0.002 wt. % to 6 wt. % respectively, relative to the entire weight of the emissive material layer. As shown in this example, the best effects were obtained particularly when the contents of vanadium and vanadium oxide were about 1.1 wt. % and about 1.3 wt. % respectively relative to the total weight of the emissive material layer.

Example 4 (not forming part of the present invention)

[0046] In the processes for manufacturing the cathode of Example 3, a mixed material was prepared by adding niobium oxide, instead of vanadium oxide, at 1 wt. % relative to barium/strontium carbonate (1.3 wt. % relative to an emissive material layer). The mixed material was adhered onto a cathode substrate in a thickness of about 50 μm , and was then thermally decomposed at 930°C in a vacuum. As a result, a cathode was provided that had an emissive material layer including barium/strontium oxide and niobium oxide.

[0047] The cathode prepared as described above

was used in a CRT for displays, and an accelerated life test was carried out for 2,000 hours while current density was set at $2.0\text{A}/\text{cm}^2$ at the beginning of the operation. Regarding the deterioration of the emission current, the same results as in the case of adding vanadium oxide were obtained, thus increasing the life of the cathode.

[0048] The cathode of this example also has the properties of limiting the heat contraction of the emissive material layer. As a result, the change in cut-off voltage was reduced. The above-noted cut-off voltage indicates the cathode voltage for cutting off emission current, and the value of the voltage changes due to the heat contraction of an emissive material layer.

[0049] FIG. 9 shows the change in cut-off voltage with time in the accelerated life test. In the figure, line G indicates the result in the case of the cathode of this example in which niobium oxide was added to the emissive material layer; and line (a) indicates the result of a conventional cathode without niobium oxide. As clearly shown in FIG. 9, the change in cut-off voltage by the accelerated life test becomes small when niobium oxide is added to the emissive material layer. In this example, niobium oxide was added to the emissive material layer, but the same results are obtained when niobium is used instead. Like vanadium, niobium and niobium oxide easily can be obtained in the industry and are also economical. Thus, by adding niobium or niobium oxide to the emissive material layer, an economical cathode is provided.

[0050] Similar to the contents of vanadium and vanadium oxide mentioned in Example 3, the contents of niobium and niobium oxide relative to the emissive material layer are 0.001 wt. % to 5 wt. % and 0.002 wt. % to 6 wt. % respectively, so that the effect of reducing the deterioration of emission current is obtained.

Example 5 (not forming part of the present invention)

[0051] In the processes for manufacturing the cathode of Example 3, a mixed material was prepared by adding tantalum oxide, instead of vanadium oxide, at 1 wt. % relative to barium/strontium carbonate (1.3 wt. % relative to an emissive material layer). The mixed material was adhered onto a cathode substrate in a thickness of about 50 μm , and was then thermally decomposed at 930°C in a vacuum. As a result, a cathode was provided that had an emissive material layer including barium/strontium oxide and tantalum oxide.

[0052] The cathode prepared as described above was used in a CRT for displays, and an accelerated life test was carried out for 2,000 hours while the current density was set at $2.7\text{A}/\text{cm}^2$ at the beginning of the operation.

[0053] FIG. 10 shows the change in emission current with time in the accelerated life test. In the figure, line H indicates the result of the cathode of this example in which tantalum oxide was added to the emissive material layer; and line (c) shows the result of a conventional

cathode. As clearly shown in FIG. 10, the cathode has a much smaller decrease in emission voltage in the accelerated life test than the conventional cathode when tantalum oxide was added to the emissive material layer, so that the life of the cathode improves. In this example, tantalum oxide was added to the emissive material layer, but the same results are obtained when tantalum is used instead.

[0054] Tantalum and tantalum oxide easily can be obtained in the industry and are also economical. Thus, by adding tantalum or tantalum oxide to the emissive material layer, an economical cathode is provided. Similar to the contents of vanadium and vanadium oxide mentioned in Example 3, the contents of tantalum and tantalum oxide relative to the emissive material layer are 0.001 wt. % to 5 wt. % and 0.002 wt. % to 6 wt. % respectively, so that the effect of limiting the decrease in emission current is obtained.

[0055] When vanadium oxide, niobium oxide or tantalum oxide are added to the emissive material layer in particle form, the decrease in emission current is found to be different depending on particle diameter. FIG. 11 shows the relationship between the average particle diameter of tantalum oxide and emission current (%) after 2,000 hours of testing, wherein the emission current is 100% at the beginning of the accelerated life test. According to the figure, the decrease in emission current was prevented effectively when the average particle diameter of tantalum oxide was 10 μm or less.

[0056] The same results were obtained when the particles of vanadium oxide or niobium oxide were added to the emissive material layer. Therefore, in adding vanadium oxide, niobium oxide or tantalum oxide into an emissive material layer in particle form, the average particle diameter is preferably 10 μm or less.

Example 6

[0057] To a nitrate solution of barium and strontium (1:1 mole ratio) containing vanadium nitrate at 0.01 mole % relative to the total amount of the nitrate in the solution, a solution of sodium carbonate was added, thus preparing the ternary coprecipitated carbonate of barium/strontium/vanadium containing vanadium at 0.01 mole %. The carbonate was adhered onto a cathode substrate in a thickness of about 50 μm , and was thermally decomposed in a vacuum at 930°C . Thus, a cathode was provided that had an emissive material layer, made of barium/strontium/vanadium oxide containing vanadium at 0.004 wt. %.

[0058] The cathode prepared as described above was used in a CRT for displays, and an accelerated life test was carried out for 2,000 hours while the current density of the CRT was set at $2.0\text{A}/\text{cm}^2$ at the beginning of the operation. FIG. 12 shows the change in emission current with time in the accelerated life test. In the figure, line I indicates the result in the case of the cathode having the emissive material layer in which vanadium was

coprecipitated.

[0059] As clearly shown in FIG. 12, the decrease in emission current in the accelerated life test becomes small when vanadium is coprecipitated in the emissive material layer, so that the life of the cathode improves. The same results were also obtained when niobium nitrate was used instead of vanadium nitrate to form an emissive material layer of a barium barium/strontium/niobium coprecipitated oxide. The effect of reducing the deterioration of emission current was obtained effectively in this example when vanadium and niobium were contained in a range of 0.001 wt. % to 1 wt. % relative to the emissive material layer.

Example 7

[0060] Into a nitrate solution of barium and strontium (1:1 mole ratio), tantalum was dissolved at 0.01 mole % relative to the whole nitrate solution. Then, a solution of sodium carbonate was added, thus preparing a coprecipitated material of tantalum and barium/strontium carbonate containing tantalum at 0.01 mole %.

[0061] The coprecipitated material was adhered onto a cathode substrate at a thickness of about 50 μm , and was thermally decomposed in a vacuum at 930°C. Thus, a cathode was provided that had an emissive material layer made of barium/strontium oxide containing tantalum at 0.014 wt. %.

[0062] The cathode prepared as described above was used in a CRT for displays, and an accelerated life test was carried out for 2,000 hours while the current density of the CRT was set at 2.7A/cm² at the beginning of the operation.

[0063] FIG. 13 shows the change in the emission current with time in the accelerated life test. In the figure, line J indicates the test result of the cathode having the emissive material layer in which tantalum was coprecipitated. As clearly shown in FIG. 13, the decrease in emission current by the accelerated life test becomes small when tantalum is coprecipitated in the emissive material layer, so that the life of the cathode increases. The effect of reducing the deterioration of the emission current was obtained effectively in this example when the content of tantalum was from 0.001 wt. % to 1 wt. % relative to the emissive material layer.

Claims

1. A cathode for a cathode ray tube having an emissive material adhered onto a metal substrate comprising nickel as a main component, characterized in that the emissive material comprises particles, wherein each particle includes an alkaline earth metal oxide as a main component and at least one element selected from the group consisting of titanium, zirconium and hafnium.

2. A cathode according to claim 1, characterized in that the emissive material comprises the element at 0.001 wt. % to 1 wt. % relative to the total weight of the emissive material.
3. A cathode according to claim 2, characterized in that the emissive material comprises the element at 0.001 wt. % to 0.1 wt. %.
4. A cathode according to claim 1, characterized in that the emissive material comprises particles consisting of an alkaline earth metal oxide.
5. A cathode according to claim 4, characterized in that the particles that include the earth metal oxide as a main component and the element are present in an amount of 20 wt. % to 80 wt. % to the total weight of the emissive material.
6. A cathode for a cathode ray tube having an emissive material adhered onto a metal substrate comprising nickel as a main component, characterized in that the emissive material comprises particles, wherein each particle includes an alkaline earth metal oxide as a main component and at least one element selected from the group consisting of vanadium, niobium and tantalum.
7. A cathode according to claim 6, characterized in that the emissive material comprises the element as a metal.
8. A cathode according to claim 7, characterized in that the emissive material comprises the metal at 0.0001 wt. % to 5 wt. % relative to the total weight of the emissive material.
9. A cathode according to claim 6, characterized in that the emissive material comprises the element as an oxide.
10. A cathode according to claim 9, characterized in that the emissive material comprises the oxide at 0.002 wt. % to 6 wt. % relative to the total weight of the emissive material.
11. A cathode according to claim 9, characterized in that the emissive material comprises the oxide as particles having an average particle diameter of 10 μm or less.
12. A method for manufacturing a cathode for a cathode ray tube, characterized in that it comprises the step of thermally decomposing carbonate comprising an alkaline earth metal and at least one element selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium and tantalum, so as to adhere an emissive material in particle form

onto a metal substrate comprising nickel as a main component, wherein each particle of the emissive material obtained from the carbonate includes an oxide of the alkaline earth metal as a main component and the element.

13. A method according to claim 12, **characterized in that** the carbonate is thermally decomposed in a vacuum.

14. A method according to claim 12, **characterized in that** it further comprises the step of coprecipitating, from a solution comprising a nitrate of at least one element selected from the group consisting of vanadium, niobium, titanium and zirconium, and a nitrate of an alkaline earth metal, the element and the alkaline earth metal as carbonate.

15. A method according to claim 14, **characterized in that** the element and the alkaline earth metal are coprecipitated as carbonate by mixing the nitrate solution with a solution comprising a carbonate ion.

16. A method according to claim 15, **characterized in that** the solution comprising a carbonate ion is a solution comprising at least one salt selected from the group consisting of carbonate of an alkaline metal, hydrogencarbonate of an alkaline metal, ammonium carbonate and ammonium hydrogencarbonate.

17. A method according to claim 12, **characterized in that** it further comprises the step of mixing a solution comprising a carbonate of an alkaline earth metal and tantalum with a solution comprising a nitrate of an alkaline earth metal so as to coprecipitate the tantalum and the alkaline earth metal as carbonate.

18. A cathode according to claims 1 or 6, **characterized in that** the particles are obtained by thermally decomposing carbonate including the alkaline earth metal and the element.

Patentansprüche

1. Kathode für eine Kathodenstrahlröhre mit einem auf einem Metallsubstrat, das Nickel als eine Hauptkomponente umfasst, haftenden Emissionsmaterial, **dadurch gekennzeichnet, dass** das Emissionsmaterial Teilchen umfasst, wobei jedes Teilchen ein Erdalkalimetalloxid als eine Hauptkomponente und wenigstens ein Element umfasst, das aus der Gruppe bestehend aus Titan, Zirkon und Hafnium ausgewählt ist.

2. Kathode gemäß Anspruch 1, **dadurch gekennzeichnet, dass** das Emissionsmaterial das Element zu 0,001 Gew.-% bis 1 Gew.-% bezogen auf das Gesamtgewicht auf das Emissionsmaterial umfasst.

3. Kathode gemäß Anspruch 2, **dadurch gekennzeichnet, dass** das Emissionsmaterial das Element zu 0,001 Gew.-% bis 0,1 Gew.-% umfasst.

4. Kathode gemäß Anspruch 1, **dadurch gekennzeichnet, dass** das Emissionsmaterial Teilchen umfasst, welche aus einem Erdalkalimetalloxid bestehen.

5. Kathode gemäß Anspruch 4, **dadurch gekennzeichnet, dass** die Teilchen, welche das Erdalkalimetalloxid als eine Hauptkomponente beinhalten, und das Element in einer Menge von 20 Gew.-% bis 80 Gew.-% zum Gesamtgewicht des Emissionsmaterials darstellen.

6. Kathode für eine Kathodenstrahlröhre mit einem auf einem Metallsubstrat, das Nickel als eine Hauptkomponente umfasst, haftenden Emissionsmaterial, **dadurch gekennzeichnet, dass** das Emissionsmaterial Teilchen umfasst, wobei jedes Teilchen ein Erdalkalimetalloxid als eine Hauptkomponente beinhaltet und wenigstens ein Element, ausgewählt aus der Gruppe, bestehend aus Vanadin, Niob und Tantal.

7. Kathode gemäß Anspruch 6, **dadurch gekennzeichnet, dass** das Emissionsmaterial das Element als ein Metall umfasst.

8. Kathode gemäß Anspruch 7, **dadurch gekennzeichnet, dass** das Emissionsmaterial das Metall zu 0,0001 Gew.-% bis 5 Gew.-% bezogen auf das Gesamtgewicht des Emissionsmaterials umfasst.

9. Kathode gemäß Anspruch 6, **dadurch gekennzeichnet, dass** das Emissionsmaterial das Element als ein Oxid umfasst.

10. Kathode gemäß Anspruch 9, **dadurch gekennzeichnet, dass** das Emissionsmaterial das Oxid zu 0,002 Gew.-% bis 6 Gew.-% bezogen auf das Gesamtgewicht des Emissionsmaterials umfasst.

11. Kathode gemäß Anspruch 9, **dadurch gekennzeichnet, dass** das Emissionsmaterial das Oxid als Teilchen mit einem mittleren Teilchen Durchmesser von 10 nm oder weniger umfasst.

12. Verfahren zur Herstellung einer Kathode für eine Kathodenstrahlröhre, **dadurch gekennzeichnet, dass** es die Stufe der thermischen Zersetzung von Carbonat, umfassend ein Erdalkalimetall und wenigstens ein Element, ausgewählt aus der Gruppe,

bestehend aus Titan, Zirkon, Hafnium, Vanadin, Niob und Tantal, umfasst, um ein Emissionsmaterial in Teilchenform auf einem Metallsubstrat, umfassend Nickel als eine Hauptkomponente, aufzubringen, wobei jedes Teilchen des Emissionsmaterials, erhalten aus dem Carbonat, ein Oxid des Erdalkalimetall als eine Hauptkomponente und das Element beinhaltet.

13. Verfahren nach Anspruch 12, **dadurch gekennzeichnet, dass** das Carbonat thermisch im Vakuum zersetzt wird.

14. Verfahren gemäß Anspruch 12, **dadurch gekennzeichnet, dass** es des Weiteren die Stufe der Copräzipitierung aus einer Lösung, umfassend ein Nitrat wenigstens eines Elementes, ausgewählt aus der Gruppe, bestehend aus Vanadin, Niob, Titan, Zirkon, und ein Nitrat eines Erdalkalimetall, das Element und das Erdalkalimetall als Carbonat, umfasst.

15. Verfahren nach Anspruch 14, **dadurch gekennzeichnet, dass** das Element und das Erdalkalimetall als Carbonat durch mischen der Nitratlösung mit einer Lösung, umfassend ein Carbonation, copräzipitiert werden.

16. Verfahren nach Anspruch 15, **dadurch gekennzeichnet, dass** die ein Carbonation umfassende Lösung eine Lösung ist, welche wenigstens ein Salz umfasst, ausgewählt aus der Gruppe, bestehend aus einem Carbonat eines Alkalimetall, einem Hydrogencarbonat eines Alkalimetall, einem Ammoniumcarbonat und einem Ammoniumhydrogencarbonat.

17. Verfahren gemäß Anspruch 12, **dadurch gekennzeichnet, dass** es des Weiteren die Stufe des Mischens einer Lösung, umfassend ein Erdalkalimetall- und Tantalcarbonat, mit einer Lösung, umfassend ein Erdalkalimetallnitrat, umfasst, um das Tantal und das Erdalkalimetall als Carbonat zu Copräzipitieren.

18. Kathode gemäß Anspruch 1 oder 6, **dadurch gekennzeichnet, dass** die Teilchen durch thermische Zersetzung von Carbonat, umfassend das Erdalkalimetall und das Element, erhalten werden.

5 particule inclut un oxyde de métal alcalino-terreux comme composant principal et au moins un élément choisi dans le groupe qui est constitué de titane, zirconium et hafnium.

2 Cathode selon la revendication 1, **caractérisée en ce que** le matériau émissif comprend l'élément à 0,001 % en poids à 1 % en poids par rapport au poids total du matériau émissif.

10 3. Cathode selon la revendication 2, **caractérisée en ce que** le matériau émissif comprend l'élément à 0,001 % en poids à 0,1 % en poids.

15 4. Cathode selon la revendication 1, **caractérisée en ce que** le matériau émissif comprend des particules qui sont constituées d'un oxyde de métal alcalino-terreux.

20 5. Cathode selon la revendication 4, **caractérisée en ce que** les particules qui incluent l'oxyde de métal terreux comme composant principal et l'élément sont présents en une teneur de 20 % en poids à 80 % en poids du poids total du matériau émissif.

25 6. Cathode pour tube à rayons cathodiques ayant un matériau émissif mis à adhérer sur un substrat métallique comprenant du nickel comme composant principal, **caractérisée en ce que** le matériau émissif comprend des particules dans lequel chaque particule inclut un oxyde de métal alcalino-terreux comme composant principal et au moins un élément choisi dans le groupe qui est constitué de vanadium, niobium et tantal.

30 7. Cathode selon la revendication 6, **caractérisée en ce que** le matériau émissif comprend l'élément comme métal.

35 8. Cathode selon la revendication 7, **caractérisée en ce que** le matériau émissif comprend le métal à 0,0001 % en poids à 5 % en poids par rapport au poids total du matériau émissif.

40 9. Cathode selon la revendication 6, **caractérisée en ce que** le matériau émissif comprend l'élément comme oxyde.

45 10. Cathode selon la revendication 9, **caractérisée en ce que** le matériau émissif comprend l'oxyde à 0,002 % en poids à 6 % en poids par rapport au poids total de matériau émissif.

50 11. Cathode selon la revendication 9, **caractérisée en ce que** le matériau émissif comprend l'oxyde comme des particules ayant un diamètre particulaire moyen de 10 µm ou moins.

Revendications

- Cathode pour tube à rayons cathodiques ayant un matériau émissif mis à adhérer sur un substrat métallique comprenant du nickel comme composant principal, **caractérisée en ce que** le matériau émissif comprend des particules, dans lequel chaque

12. Procédé pour fabriquer une cathode pour un tube à rayons cathodiques, caractérisé en ce qu'il comprend l'étape consistant à décomposer thermiquement le carbonate comprenant un métal alcalino-terreux et au moins un élément choisi dans le groupe constitué de titane, zirconium, hafnium, vanadium, niobium et tantale, de façon à mettre à adhérer un matériau émissif sous forme particulaire sous un substrat métallique comprenant du nickel comme composant principal, dans lequel chaque particule du matériau émissif obtenu à partir du carbonate inclut un oxyde du métal alcalino-terreux comme composant principal et l'élément. 5

13. Procédé selon la revendication 12, caractérisé en ce que le carbonate est décomposé thermiquement sous vide. 15

14. Procédé selon la revendication 12, caractérisé en ce qu'il comprend, en outre, l'étape consistant à coprécipiter, à partir d'une solution comprenant un nitrate d'au moins un élément choisi dans le groupe qui est constitué de vanadium, niobium, titane et zirconium, et un nitrate d'un métal alcalino-terreux, l'élément et le métal alcalino-terreux comme carbonate. 20 25

15. Procédé selon la revendication 14, caractérisé en ce que l'élément et le métal alcalino-terreux sont coprécipités comme carbonate en mélangeant la solution de nitrate avec une solution comprenant un ion carbonate. 30

16. Procédé selon la revendication 15, caractérisé en ce que la solution comprenant un ion carbonate est une solution comprenant au moins un sel choisi dans le groupe qui est constitué du carbonate d'un métal alcalin, de l'hydrogénocarbonate d'un métal alcalin, du carbonate d'ammonium et de l'hydrogénocarbonate d'ammonium. 35 40

17. Procédé selon la revendication 12, caractérisé en ce qu'il comprend, en outre, l'étape consistant à mélanger une solution comprenant un carbonate d'un métal alcalino-terreux et du tantale à une solution comprenant un nitrate d'un métal alcalino-terreux de façon à coprécipiter le tantale et le métal alcalino-terreux comme carbonate. 45

18. Cathode selon la revendication 1 ou 6, caractérisée en ce que les particules sont obtenues en décomposant thermiquement le carbonate incluant le métal alcalino-terreux et l'élément. 50

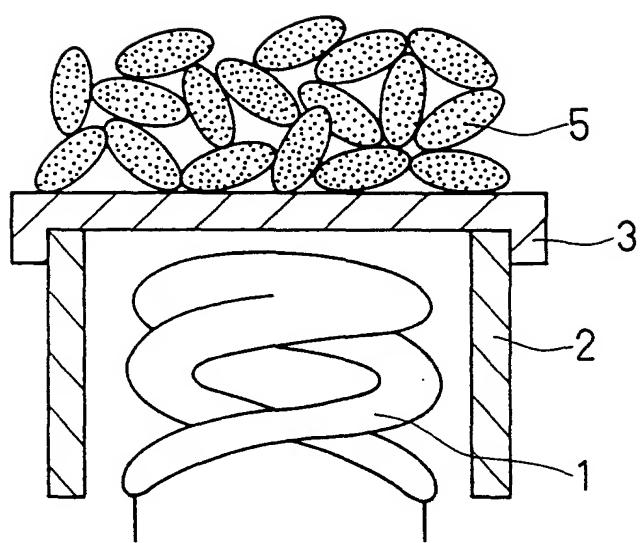


FIG. 1

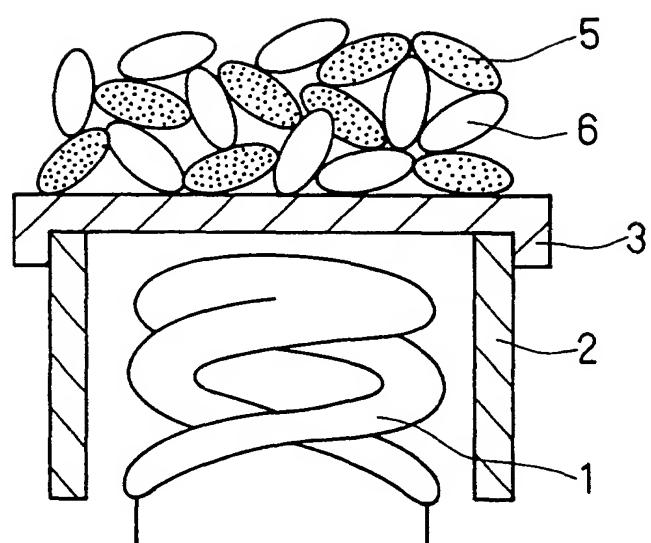


FIG. 2

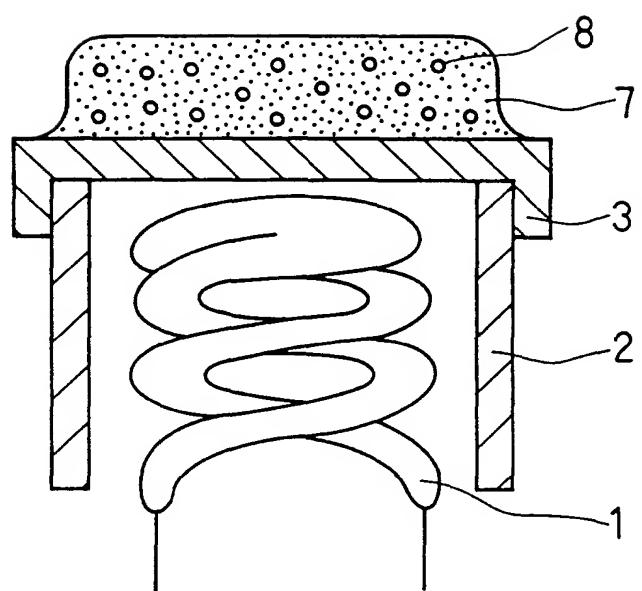


FIG. 3

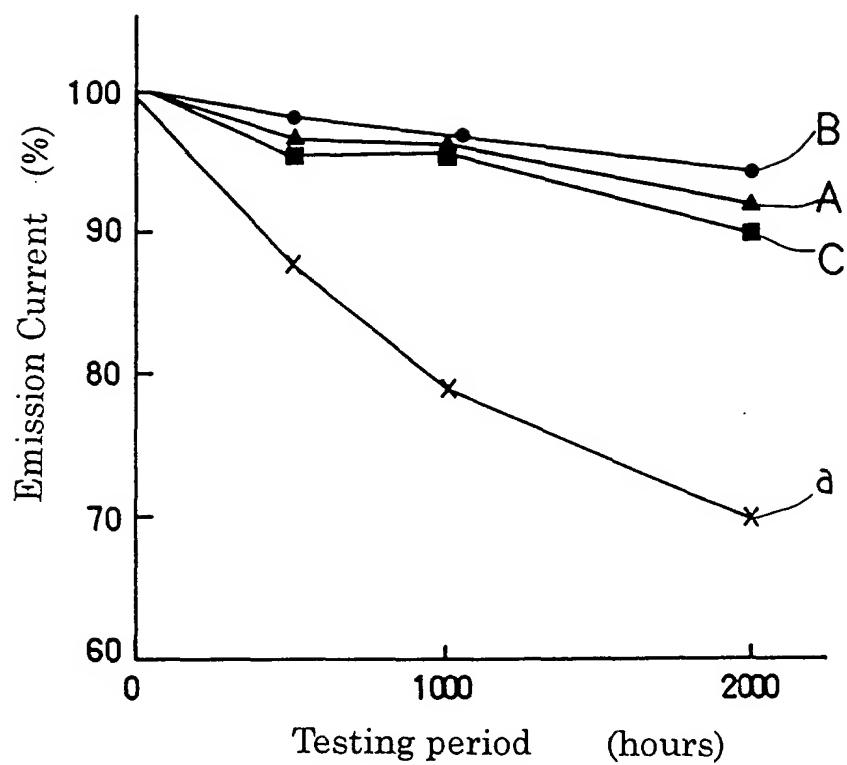


FIG . 4

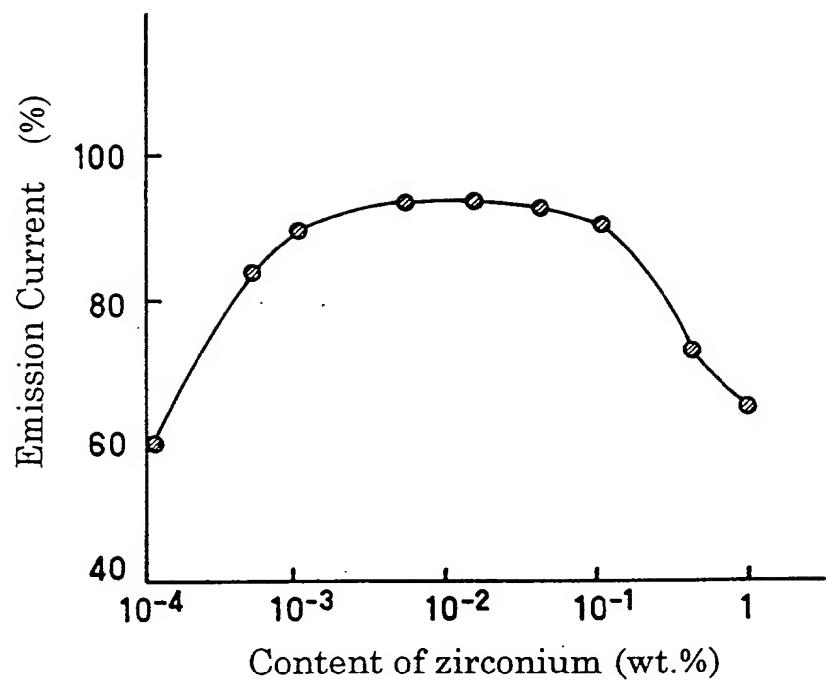


FIG. 5

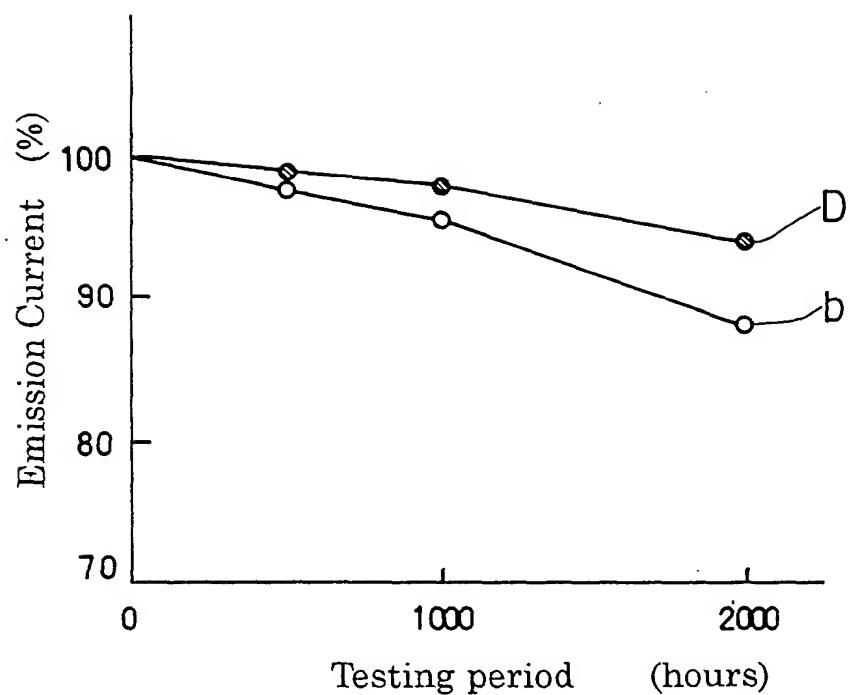


FIG. 6

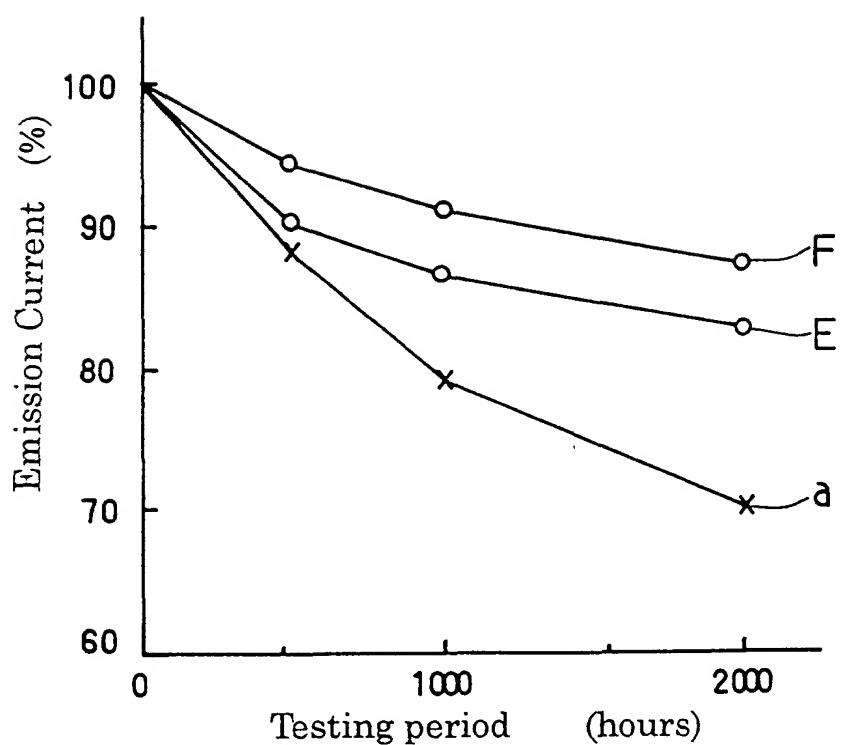


FIG . 7

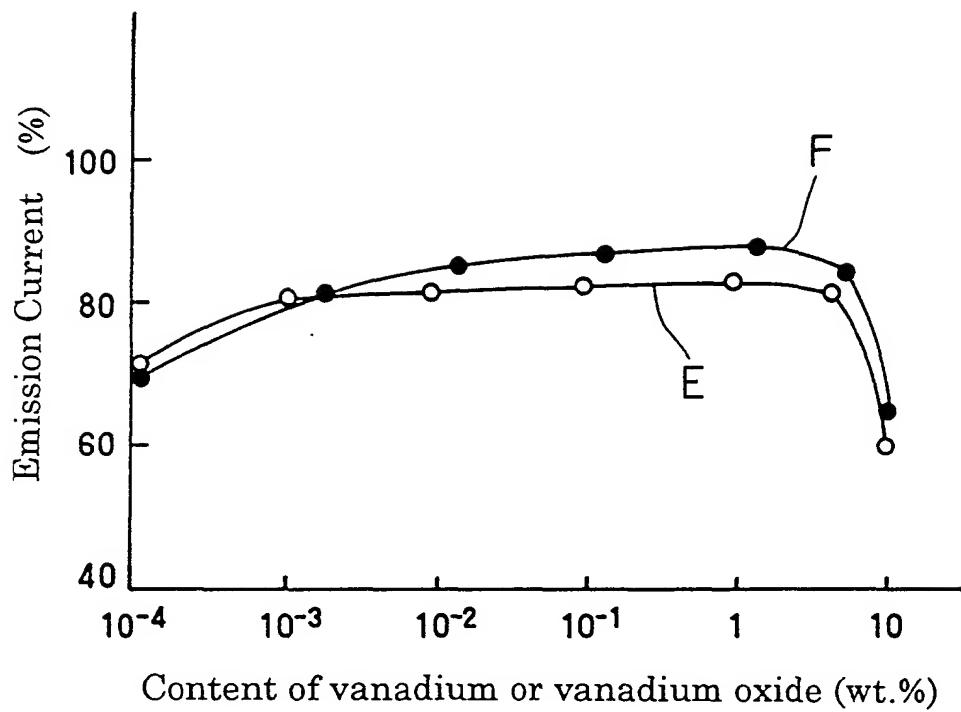


FIG. 8

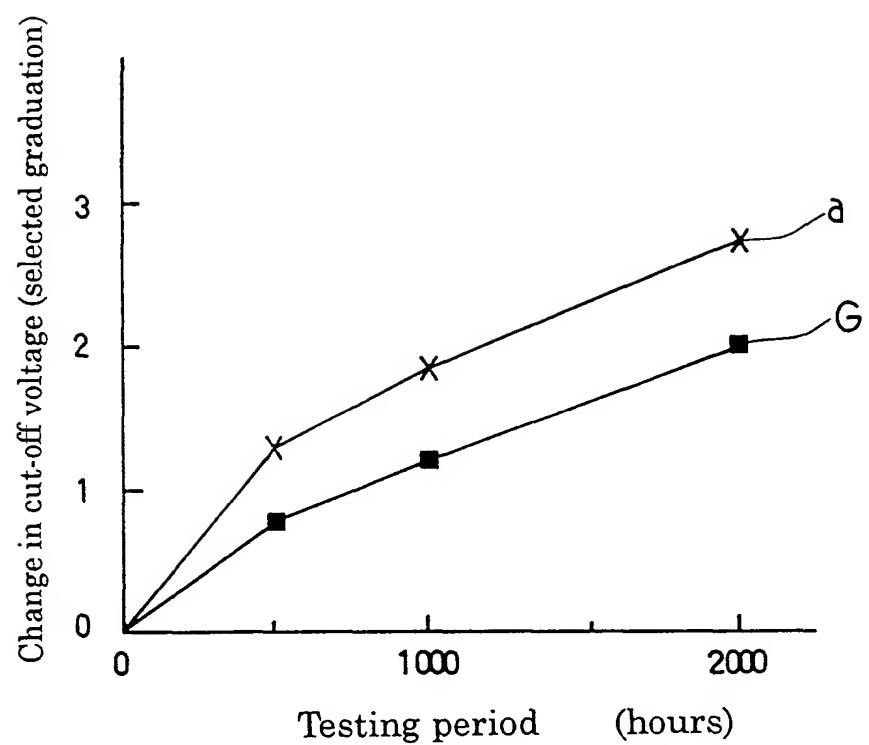


FIG. 9

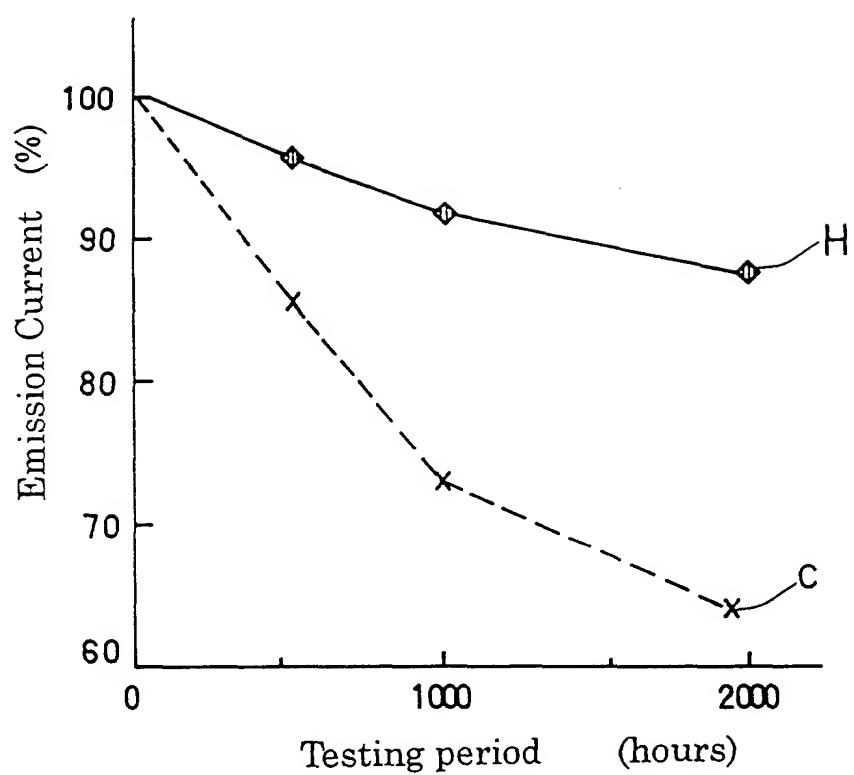


FIG. 10

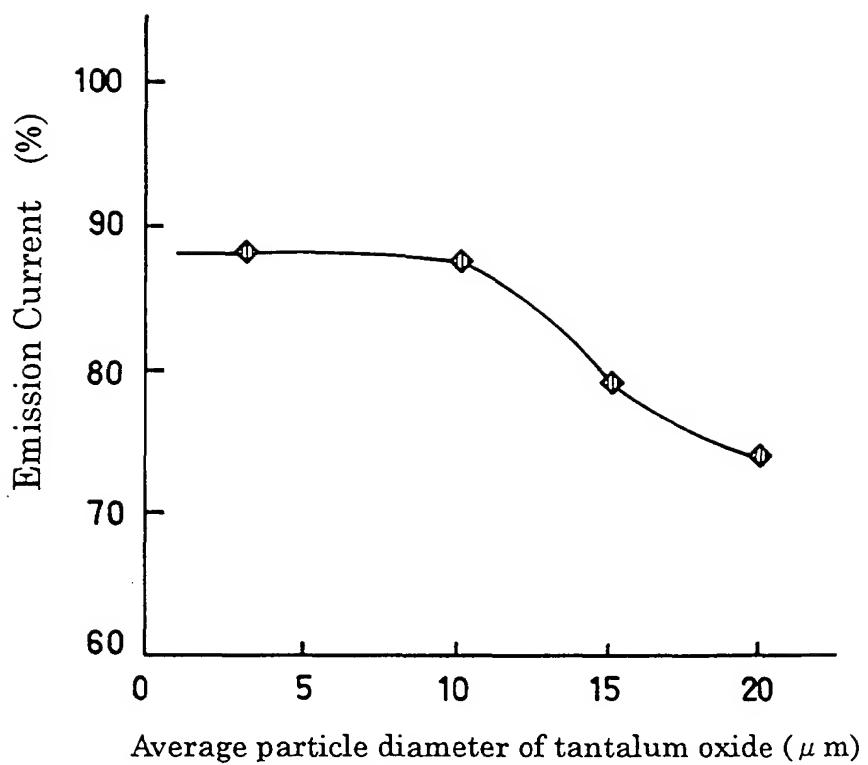


FIG. 11

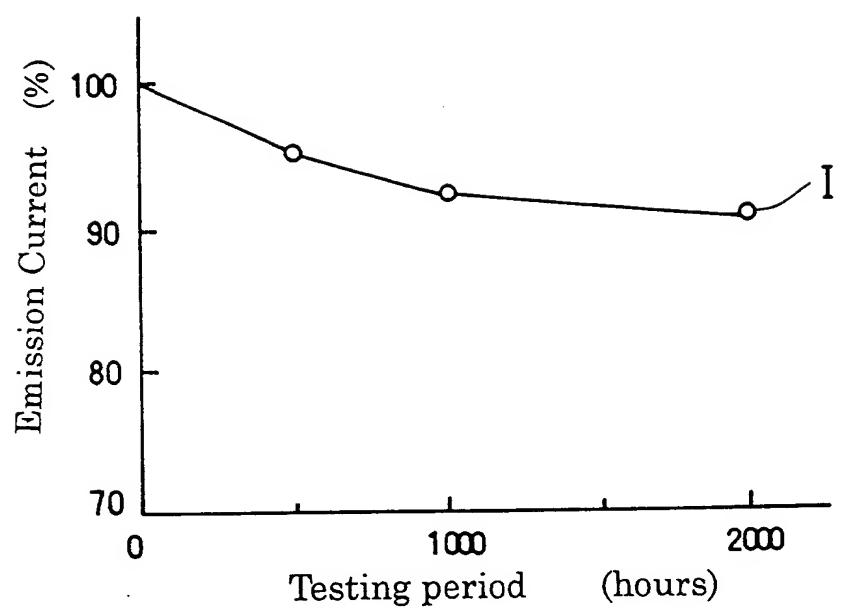


FIG. 12

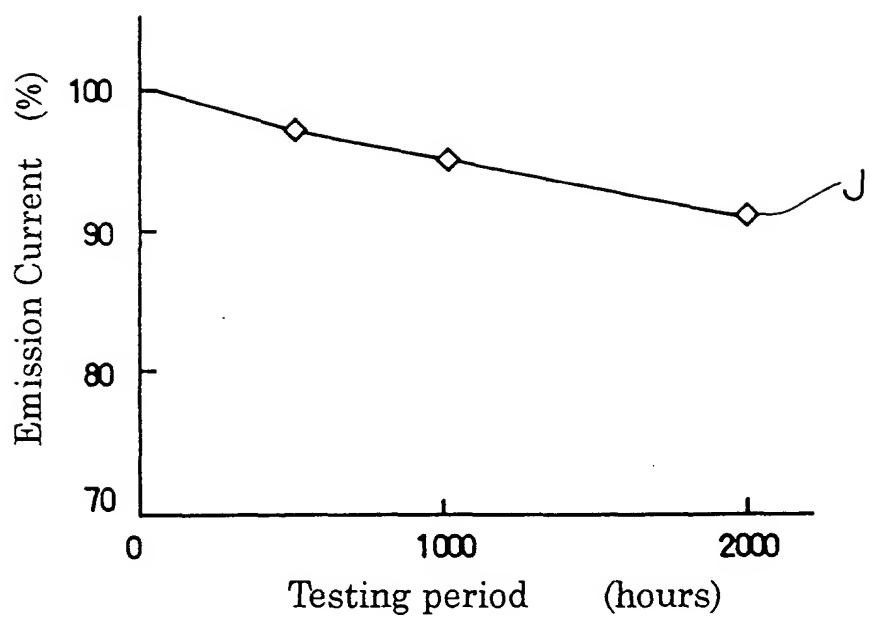


FIG. 13

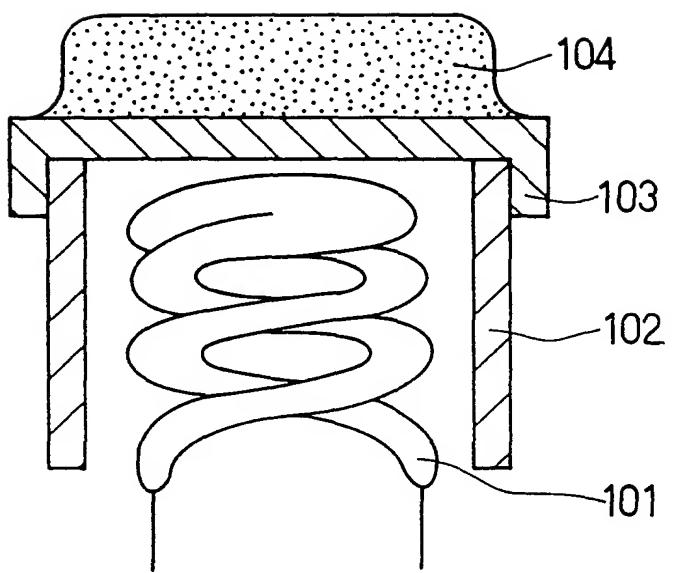


FIG. 14